

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C22C 1/04, C22F 1/06	A1	(11) International Publication Number: WO 91/13181 (43) International Publication Date: 5 September 1991 (05.09.91)
(21) International Application Number: PCT/US91/01048 (22) International Filing Date: 18 February 1991 (18.02.91) (30) Priority data: 481,402 20 February 1990 (20.02.90) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (72) Inventors: DAS, Santosh, K. ; 10 Farm Road, Randolph, NJ 07869 (US). CHANG, Chin-Fong ; 595 Lynne Drive, Morris Plains, NJ 07950 (US). RAYBOULD, Derek ; 2 Horizon Drive, Denville, NJ 07834 (US).		(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD FOR SUPERPLASTIC FORMING OF RAPIDLY SOLIDIFIED MAGNESIUM BASE METAL ALLOYS (57) Abstract A complex part composed of rapidly solidified magnesium base metal alloy is produced by superplastic forming at a temperature ranging from 160 °C to 275 °C and at a rate ranging from 0.00021 m/sec to 0.00001 m/sec, to improve the formability thereof and allow forming to be conducted at lower temperature. The rapidly solidified magnesium based alloy has a composition consisting essentially of the formula $Mg_{ba}Al_aZn_bX_c$, wherein X is at least one element selected from the group consisting of manganese, cerium, neodymium, praseodymium and yttrium, "a" ranges from 0 to about 15 atom percent, "b" ranges from 0 to about 4 atom percent and "c" ranges from about 0.2 to 3 atom percent, the balance being magnesium and incidental impurities, with the proviso that the sum of aluminum and zinc present ranges from about 2 to 15 atom percent. Such an alloy contains fine grain size and finely dispersed magnesium-, aluminum- rare earth intermetallic phases. When formed, the part exhibits good corrosion resistance together with high ultimate tensile strength and good ductility at room temperature, which properties are, in combination, far superior to those of conventional magnesium alloys. The part is suitable for application as a structural member in helicopters, missiles and air frames where good corrosion resistance in combination with high strength and ductility is important.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

- 1 -

**METHOD FOR SUPERPLASTIC FORMING OF RAPIDLY
SOLIDIFIED MAGNESIUM BASE METAL ALLOYS**

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of
U.S. Application Serial No. 197,796, filed May 23,
1988.

1. Field of Invention

 This invention relates to a method for
10 superplastic forming (extrusion, forging, and
rolling, etc.) of bulk articles made by consolidation
of the powder of rapidly solidified magnesium base
metal alloys, to achieve a combination of good
formability to complex net shapes and good mechanical
15 properties of the articles. The superplastic forming
allows deformation to near net shapes.

2. Description of the Prior Art

 Magnesium alloys are considered attractive
candidates for structural use in aerospace and
20 automotive industries because of their light weight,
high strength to weight ratio, and high specific
stiffness at both room and elevated temperatures.
Although magnesium has reasonable corrosion
properties under regular atmospheric conditions, it
25 is susceptible to attack by chloride containing
environments. Furthermore, the high chemical
reactivity of magnesium, as represented by its
extreme position in the electrochemical series and
its inability to form a protective, self-healing,
30 passive film in corrosive environments, makes
magnesium alloys vulnerable to galvanic attack when
coupled with more noble metals. In addition to the
galvanic coupling between the structural members,
localized corrosion may occur due to inhomogeneities
35 within the magnesium alloy that act as electrodes for
galvanic corrosion. This poor corrosion resistance

- 2 -

of magnesium has been a serious limitation, preventing wide scale use of magnesium alloys.

The application of rapid solidification processing (RSP) in metallic system results in the refinement of grain size and intermetallic particle size, extended solid solubility, and improved chemical homogeneity. By selecting the thermally stable intermetallic compound (Mg_2Si) to pin the grain boundary during consolidation, a significant improvement in the mechanical strength [0.2% yield strength (Y.S.) up to 393 MPa, ultimate tensile strength (UTS) up to 448 MPa, elongation (El.) up to 9%] can be achieved in RSP Mg-Al-Zn-Si alloys, [S.K. Das, et al., U.S. Pat. No. 4,675,157, High Strength Rapidly Solidified Magnesium Base Metal Alloys, June 1987]. The addition of rare earth elements (Y, Nd, Pr, Ce) to Mg-Al-Zn alloys further improves corrosion resistance (11 mdd when immersed in 3% NaCl aqueous solution for 3.4×10^5 sec. at 27°C) and mechanical properties (Y.S. up to 435 MPa, U.T.S. up to 476 MPa, El. up to 14%) of magnesium alloys [S.K. Das and C.F. Chang, U.S. Pat. No. 4,765,954, Rapidly Solidified High Strength Corrosion Resistant Magnesium Base Metal Alloys, August 1988]. The alloys are subjected to rapid solidification processing by using a melt spin casting method wherein the liquid alloy is cooled at a rate of 10^5 to 10^7 °C/sec while being solidified into a ribbon or sheet. That process further comprises the provision of a means to protect the melt puddle from burning, excessive oxidation and physical disturbance by the air boundary layer carried with the moving substrate. The protection is provided by a shrouding apparatus which serves the dual purpose of containing a protective gas such as a mixture of air or CO_2 and SF_6 , a reducing gas such as CO or an inert gas, around the nozzle while excluding extraneous wind currents which may disturb the melt

- 3 -

puddle. The as cast ribbon or sheet is typically 25 to 100 μm thick. The rapidly solidified ribbons are sufficiently brittle to permit them to be mechanically comminuted by conventional apparatus, such as a ball mill, knife mill, hammer mill, pulverizer, fluid energy mill. The comminuted powders are either vacuum hot pressed to about 95% dense cylindrical billets or directly canned to similar size. The billets or cans are then hot extruded to round or rectangular bars at an extrusion ratio ranging from 14:1 to 22:1.

Magnesium alloys, like other alloys with hexagonal crystal structures, are much more workable at elevated temperatures than at room temperature. The basic deformation mechanisms in magnesium at room temperature involve both slip on the basal planes along $\langle 1,1,-2,0 \rangle$ directions and twinning in planes $(1,0,1,2)$ and $\langle 1,0,-1,1 \rangle$ direction. At higher temperatures ($>225^\circ\text{C}$), pyramidal slip $(1,0,-1,1)$ $\langle 1,1,-2,0 \rangle$ becomes operative. The limited number of slip systems in the hcp magnesium presents plastic deformation conformity problems during working of a polycrystalline material. This results in cracking unless substantial crystalline rotations of grain boundary deformations are able to occur. For the fabrication of formed magnesium alloy parts, the temperature range between the minimum temperature to avoid cracking and a maximum temperature to avoid softening is quite narrow. The forgeability of conventional processed magnesium alloys depends on three factors: the solidus temperature of the alloy, the deformation rate, and the grain size. Magnesium alloys are often forged within 55°C (100°F) of their solidus temperature [Metals Handbook, Forming and Forging, Vol. 14, 9th ed., ASM International, 1988, pp. 259-260]. An exception is the high-zinc alloy ZK60, which sometimes contains small amounts of the

- 4 -

low melting eutectic that forms during ingot solidification. Forging of this alloy above about 315°C (600°F) - the melting point of the eutectic - can cause severe cracking. The problem can be

5 minimized by holding the cast ingot for extended periods at an elevated temperature to dissolve the eutectic and to restore a higher solidus temperature. The mechanical properties developed in magnesium forgings depend on the strain hardening

10 induced during forging. Strain hardening can be achieved by keeping the forging temperature as low as practical; however, if temperatures are too low, cracking will occur. Work on metalworking of formed magnesium parts made from rapidly solidified

15 magnesium alloys is relatively rare. Busk and Leontis [R.S. Busk and T.I. Leontis, "The Extrusion of Powdered Magnesium Alloys", Trans. AIME, 188 (2) (1950), pp. 297-306] investigated hot extrusion of atomized powder of a number of commercial magnesium

20 alloys in the temperature range of 316°C (600°F) - 427°C (800°F). The as-extruded properties of alloys extruded from powder were not significantly different from the properties of extrusions from permanent mold billets. In the study reported by Isserow and

25 Rizzitano [S. Isserow and F.J. Rizzitano, "Microquenched Magnesium ZK60A Alloy", Inten'l J. of Powder Metallurgy and Powder Technology, 10 (3) (1974), pp. 217-227.] on commercial ZK60A magnesium alloy powder made by rotating electrode process

30 extrusion temperatures varying from ambient to 371°C (700°F) were used. The mechanical properties of the room temperature extrusions were significantly better than those obtained by Busk and Leontis but those extruded at 121°C (250°F) did not show any

35 significant difference between the conventionally processed and rapidly solidified material. However, care must be exercised in comparing their mechanical

- 5 -

properties in the longitudinal direction from room temperature extrusions since they observed significant delamination on the fracture surfaces; and properties may be highly inferior in the
5 transverse direction.

There remains a need in the art for the economic production of complex net shape articles consolidated from rapidly solidified magnesium alloys, particularly containing uniform dispersions
10 of intermetallic compounds that provide the alloys with good corrosion resistance combined with high strength and good ductility.

Summary of the Invention

The present invention provides a method of
15 making a superplastic forming metal complex net shape article fabricated from a high strength, corrosion resistant magnesium based alloy. The alloy is rapidly solidified into ribbon or powder and which is especially suited for consolidation into bulk shapes
20 having a fine microstructure. Generally stated, the alloy has a composition consisting essentially of the formula $Mg_{ba1}Al_aZn_bX_c$, wherein X is at least one element selected from the group consisting of manganese, cerium, neodymium, praseodymium, and
25 yttrium, "a" ranges from about 0 to 15 atom percent, "b" ranges from about 0 to 4 atom percent, "c" ranges from about 0.2 to 3 atom percent, the balance being magnesium and incidental impurities, with the proviso that the sum of aluminum and zinc present ranges from
30 about 2 to 15 atom percent.

The magnesium alloys used in the forming of the present invention are subjected to rapid solidification processing by using a melt spin casting method wherein the liquid alloy is cooled at
35 a rate of 10^5 to 10^7 °C/sec while being formed into a solid ribbon or sheet. That process further comprises the provision of a means to protect the

- 6 -

melt puddle from burning, excessive oxidation and physical disturbance by the air boundary layer carried with the moving substrate. Said protection is provided by a shrouding apparatus which serves the
5 dual purpose of containing a protective gas such as a mixture of air or CO_2 and SF_6 , a reducing gas such as CO or an inert gas, around the nozzle while excluding extraneous wind currents which may disturb the melt puddle.

10 The alloy elements manganese, cerium, neodymium, praseodymium and yttrium, upon rapid solidification processing, form a fine uniform dispersion of intermetallic phases such as Mg_3Ce , Al_2Nd , Mg_3Pr , Al_2Y , depending on the alloy
15 composition. These finely dispersed intermetallic phases increase the strength of the alloy and help to maintain a fine grain size by pinning the grain boundaries during consolidation of the powder at elevated temperature. The addition of the alloying
20 elements aluminum and zinc contributes to strength via matrix solid solution strengthening and by formation of certain age hardening precipitates such as $\text{Mg}_{17}\text{Al}_{12}$ and MgZn .

In accordance with the present invention, the
25 forming is produced from a consolidated metal alloy article. Consolidation of the article is made by compacting powder particles of the magnesium based alloy with or without canning, and degassing. The powder particles can be warm pressed by heating in a
30 vacuum to a pressing temperature ranging from 150°C to 275°C , which minimizes coarsening of the dispersed, intermetallic phases. These powder particles can be formed into bulk shapes using conventional methods such as extrusion. The present
35 invention provides a method of metal working of formed magnesium parts to complex net shape by forging and superplastic forming (at a rate ranging

- 7 -

from 0.00021 m/sec to 0.00001 m/sec, and at a temperature ranging from 160°C to 275°C).

Consolidated metal articles made from magnesium based alloys by the process described herein above exhibit good corrosion resistance (i.e., corrosion rate of less than 50 mils per year when immersed in a 3 percent NaCl aqueous solution at 25°C for 96 hours) together with high ultimate tensile strength [up to 513 MPa (74.4 ksi)] and good ductility (i.e., >5 percent tensile elongation) at room temperature. These properties present in superplastic formings produced from the consolidated articles, are, in combination, far superior to those of conventional magnesium alloy. The formings are suitable for applications as structural members in helicopters, missiles and air frames where good corrosion resistance in combination with high strength and ductility is important.

Brief Description of the Drawings

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description and the accompanying drawings, in which:

Fig. 1(a) is a transmission electron micrograph of as-cast ribbon of the alloy $Mg_{92}Zn_2Al_5Ce_1$ illustrating the fine grain size and precipitates thereof;

Fig. 1(b) is a transmission electron micrograph of as-cast ribbon of the alloy $Mg_{91}Zn_2Al_5Y_2$;

Fig. 2(a) is a transmission electron micrograph of as-extruded bulk compact of alloy $Mg_{92}Zn_2Al_5Ce_1$;

Fig. 2(b) is a transmission electron micrograph of as-extruded bulk compact of alloy $Mg_{91}Zn_2Al_5Y_2$ illustrating the fine grain and dispersoid size retained after compaction;

- 8 -

Fig. 3(a) is a micrograph of a forging consolidated from an alloy $Mg_{92}Zn_2Al_5Nd_1$ at a temperature of 180°C and at a moderate rate; and

Fig. 3(b) is a micrograph of a forging consolidated from an alloy $Mg_{92}Zn_2Al_5Nd_1$ at a temperature of 160°C and at a low rate illustrating the effect of strain rate on the superplastic formability of the alloy.

Detailed Description of the Invention

10 And the Preferred Embodiments

In accordance with the present invention a forming is produced from an article consolidated from a rapidly solidified alloy. The alloy consists essentially of nominally pure magnesium alloyed with
15 about 0 to 15 atom percent aluminum, about 0 to 4 atom percent zinc, about 0.2 to 3 atom percent of at least one element selected from the group consisting of manganese, cerium, neodymium, praseodymium, and yttrium, the balance being magnesium and incidental
20 impurities, with the proviso that the sum of aluminum and zinc present ranges from about 2 to 15 atom percent. The alloy is melted in a protective environment; and quenched in a protective environment at a rate of at least about 10^5 °C/sec by directing
25 the melt into contact with a rapidly moving chilled surface to form thereby a rapidly solidified ribbon. Such alloy ribbons have high strength and high hardness (i.e., microVickers hardness of at least about 125 kg/mm²). When aluminum is alloyed without
30 addition of zinc, the minimum aluminum content is preferably above about 6 atom percent.

The alloys of the consolidated article from which the forming of the invention is produced have a very fine microstructure which is not resolved by
35 optical micrograph. Transmission electron micrograph reveals a substantially uniform cellular network of solid solution phase ranging from 0.2-1.0 μm in size,

- 9 -

together with precipitates of very fine, binary or ternary intermetallic phases which are less than 0.1 μm and composed of magnesium and other elements added in accordance with the invention.

5 The mechanical properties [e.g. 0.2% yield strength (YS) and ultimate tensile strength (UTS)] of the alloys of this invention are substantially improved when the precipitates of the intermetallic phases have an average size of less than 0.1 μm , and
10 even more preferably an average size ranging from about 0.03 to 0.07 μm . The presence of intermetallic phases precipitates having an average size less than 0.1 μm pins the grain boundaries during consolidation of the powder at elevated temperature with the result
15 that a fine grain size is substantially maintained during high temperature consolidation.

 In Figs. 1(a) and 1(b) there are illustrated the microstructures of ribbon cast from alloys consisting essentially of the compositions
20 $\text{Mg}_{92}\text{Zn}_2\text{Al}_5\text{Ce}_1$ and $\text{Mg}_{91}\text{Zn}_2\text{Al}_5\text{Y}_2$, respectively. The microstructures shown are typical of samples solidified at cooling rate in excess of $10^5^\circ\text{C}/\text{sec}$ and is responsible for high hardness ranging from 140-200 kg/mm^2 . The high hardness of Mg-Al-Zn-X alloys can
25 be understood by the fine microstructure observed in as-cast ribbons. The as-cast microstructure of alloys containing Ce, Pr and Nd are very similar and show a cellular microstructure with precipitation of Mg_3X ($\text{X} = \text{Ce}, \text{Pr}$) both inside the cell and at cell
30 boundaries (Fig. 1a). The alloy containing Y and Nd shows fine spherical precipitates of Al_2X ($\text{X} = \text{Y}, \text{Nd}$) dispersed uniformly throughout Fig. 1(b).

 The as cast ribbon or sheet is typically 25 to 100 μm thick. The rapidly solidified materials of
35 the above described compositions are sufficiently brittle to permit them to be mechanically comminuted by conventional apparatus, such as a ball mill, knife

- 10 -

mill, hammer mill, pulverizer, fluid energy mill, or the like. Depending on the degree of pulverization to which the ribbons are subjected, different particle sizes are obtained. Usually the powder
5 comprises of platelets having an average thickness of less than 100 μm . These platelets are characterized by irregular shapes resulting from fracture of the ribbon during comminution.

The powder can be consolidated into fully
10 dense bulk parts by known techniques such as hot isostatic pressing, hot rolling, hot extrusion, hot forging, cold pressing followed by sintering, etc. Typically, the comminuted powders of the alloys are either vacuum hot pressed to cylindrical billets with
15 diameters ranging from 50 mm to 110 mm and length ranging from 50 mm to 140 mm or directly canned up to 280 mm in diameter. The billets or cans are then hot extruded to round or rectangular bars having an extrusion ratio ranging from 14:1 to 22:1 at a rate
20 ranging from 0.00021 m/sec to 0.00001 m/sec. Generally, each of the extruded bars has a thickness of at least 6 mm measured in the shortest dimension, and is capable of being subsequently hot rolled to 1 mm thick plate. The extrusion temperature normally
25 ranges from 150°C to 275°C. The extruded bars can also be fabricated into complex smooth shape with a thickness of at least 1 mm measured along the shortest direction by superplastic forming at a rate ranging from 0.00021 m/sec to 0.00001 m/sec. The
30 superplastic forming temperature ranges from 160°C to 275°C. It was surprisingly found that superplastic forming of this hcp metal is possible and that superplastic forming of these alloys allows lower forming/forging temperatures than conventional
35 forming/forging temperatures.

The microstructure obtained after consolidation depends upon the composition of the

- 11 -

alloy and the consolidation conditions. Excessive times at high temperatures can cause the fine precipitates to coarsen beyond the optimal submicron size, leading to a deterioration of the properties, i.e., a decrease in hardness and strength. Hence, the ability of superplastic forming at lower temperatures than conventional forming offers the opportunity to refine the microstructure and increase the strength.

As representatively shown in Figs. 2(a) and 2(b) for alloys $Mg_{92}Zn_2Al_5Ce_1$ and $Mg_{91}Zn_2Al_5Y_2$, respectively, the compacted consolidated article of the invention is composed of a magnesium solid solution phase having an average grain size of 0.5 μm , containing a substantially uniform distribution of dispersed intermetallic phase Mg_3X ($X = Ce, Pr$), Al_2Nd , or Al_2Y , depending on the alloy and in addition, the microstructure contains aluminum containing precipitates of phase $Mg_{17}Al_{12}$ and zinc containing phase $MgZn$. Both $Mg_{17}Al_{12}$ and $MgZn$ phases are usually larger than the Mg_3X phase and is 0.5 to 1.0 μm in size depending on consolidation temperature.

At room temperature (about 20°C), the compacted, consolidated article has a Rockwell B hardness of at least about 55 and is more typically higher than 65. Additionally, the ultimate tensile strength of the consolidated article from which the forming of the invention is produced is at least about 378 MPa (55 ksi). The high strengths [0.2% YS up to 456 MPa (66.2 ksi) and UTS up to 513 MPa (74.4 ksi)] of the alloys at room temperature, fall to two-thirds [0.2% YS = 250-330 MPa (36.3-48.0 ksi) UTS = 300-380 MPa (43.6-55.2 ksi)] of their room temperature values when tested at 100°C and drop to one-third or one-quarter (0.2% YS = 110-160 MPa (16.0-23.2 ksi), UTS = 140-190 MPa (20.3-27.6 ksi)] of their room temperature values on testing at

- 12 -

150°C. These reductions in strength are accompanied by 10-40 fold increases in elongation to fracture at 100°C (elongation 45-65%) and 150°C (elongation 190-220%), respectively, and with strength levels at 5 150°C comparable with wrought ingot alloys ZK60 and AZ91HP. The mechanical properties of the consolidated article also strongly depend on the strain rate. At a constant temperature increasing the strain rate increases the tensile strength. 10 Moreover, the strain rate dependence of strength increases with increasing temperature. Testing at a high temperature and a low strain rate tends to improve the ductility. Superplastic behavior (elongation > 100%) occurred at a test temperature of 15 150°C and at a strain rate $< 1 \times 10^{-3}$ /sec. in the consolidated article. The combination of low flow stress and high ductility in the alloys makes them exceptionally useful in superplastic forming such as hot rolling and hot forging. When forged in a close 20 die at a low rate, a complex part may be formed in a single step and with outstanding precision of shape and no cracks. The very low flow stress of these alloys at a low strain rate means that such forgings can be produced in light presses at a temperature as 25 low as 160°C.

The following examples are presented in order to provide a more complete understanding of the invention. The specific techniques, conditions, materials and reported data set forth to illustrate 30 the invention are exemplary and should not be construed as limiting the scope of the invention.

EXAMPLE 1

Ribbons samples were cast in accordance with the procedure described above by using an over 35 pressure of argon or helium to force molten magnesium alloy through the nozzle onto a water cooled copper alloy wheel rotated to produce surface speeds of

- 13 -

between about 900 m/min and 1500 m/min. Ribbons were 0.5-2.5 cm wide and varied from about 25 to 100 μ m thick.

The nominal compositions of the alloys based on the charge weight added to the melt are summarized in Table 1 together with their as-cast hardness values. The hardness values are measured on the ribbon surface which is facing the chilled substrate; this surface being usually smoother than the other surface. The microhardness of these Mg-Al-Zn-X alloys used in the forming of the present invention ranges from 140 to 200 Kg/mm². The as-cast hardness increases as the rare earth content increases. The hardening effect of the various rare earth elements on Mg-Zn-Al-X alloys is comparable. For comparison, also listed in Table 1 is the hardness of a commercial corrosion resistant high purity magnesium AZ91C-HP alloy. It can be seen that the hardness of the alloys used in the forming of the present invention is higher than commercial AZ91C-HP alloy.

TABLE 1

Microhardness (Kg/mm²) Values of
R.S. Mg-Al-Zn-X As Cast Ribbons

Sample	Alloy	Hardness
25	Nominal (At %)	
1	Mg _{92.5} Zn ₂ Al ₅ Ce _{0.5}	151
2	Mg ₉₂ Zn ₂ Al ₅ Ce ₁	186
3	Mg _{92.5} Zn ₂ Al ₅ Pr _{0.5}	150
4	Mg ₉₁ Zn ₂ Al ₅ Y ₂	201
30 5	Mg ₈₈ Al ₁₁ Mn ₁	162
6	Mg _{88.5} Al ₁₁ Mn _{0.5}	140
7	Mg ₉₂ Zn ₂ Al ₅ Nd ₁	183
<u>Alloy Outside The Scope Of The Invention</u>		
Commercial Alloy AZ 91C-HP		
35 8	(Mg _{91.7} Al _{8.0} Zn _{0.2} Mn _{0.1})	116

- 14 -

EXAMPLE 2

Rapidly solidified ribbons were subjected first to knife milling and then to hammer milling to produce -40 mesh powders. The powders were vacuum
5 outgassed and hot pressed at 200-275°C. The compacts were extruded at temperatures of about 200-250°C at extrusion ratios ranging from 14:1 to 22:1. The compacts were soaked at the extrusion temperature for about 20 mins. to 4 hours. Tensile samples were
10 machined from the extruded bulk compacted bars and tensile properties were measured in uniaxial tension at a strain rate of about 5.5×10^{-4} /sec at room temperature. The tensile properties together with Rockwell B (R_B) hardness measured at room temperature
15 are summarized in Table 2. The alloys show high hardness ranging from 65 to about 81 R_B .

Most commercial magnesium alloys have a hardness of about 50 R_B . The density of the bulk compacted samples measured by conventional Archimedes
20 technique is also listed in Table 2.

Both the yield strength (YS) and ultimate tensile strength (UTS) of the present alloys are exceptionally high. For example, the alloy $Mg_{91}Zn_2Al_5Y_2$ has a yield strength of 66.2 Ksi and UTS
25 of 74.4 Ksi which is similar to that of conventional aluminum alloys such as 7075, and approaches the strength of some commercial low density aluminum-lithium alloys. The density of the magnesium alloys is only 1.93 g/c.c. as compared with
30 a density of 2.75 g/c.c. for conventional aluminum alloys and 2.49 g/c.c. for some of the advanced low density aluminum lithium alloys now being considered for aerospace applications. Thus, on a specific strength (strength/density) basis the magnesium base
35 alloys provide a distinct advantage in aerospace applications. In some of the alloys ductility is quite good and suitable for engineering

- 15 -

applications. For example, $Mg_{91}Zn_2Al_5Y_2$ has a yield strength of 66.2 Ksi, UTS of 74.4 Ksi, and elongation of 5.0%, which is superior to the commercial alloys ZK60A, and AZ91C-HP, when combined strength and ductility is considered. The magnesium base alloys find use in military applications such as sabots for armor piercing devices, and air frames where high strength is required.

TABLE 2

10 Room Temperature Properties of Rapidly Solidified
Mg-Al-Zn-X Alloy Extrusions

	Composition Nominal (AT%)	Density (g/c.c.)	Hardness (R_p)	Y.S. MPa(Ksi)	U.T.S. MPa(Ksi)	Elong. (%)
	$Mg_{92.5}Zn_2Al_5Ce_{0.5}$	1.89	66	359 (52.1)	425 (61.7)	17.5
15	$Mg_{92}Zn_2Al_5Ce_1$	1.93	77	425 (61.7)	487 (70.6)	10.1
	$Mg_{92.5}Zn_2Al_5Pr_{0.5}$	1.89	65	352 (51.1)	427 (61.9)	15.9
	$Mg_{91}Zn_2Al_5Y_2$	1.93	81	456 (66.2)	513 (74.4)	5.0
	$Mg_{88}Al_{11}Mn_1$	1.81	66	373 (54.2)	391 (56.8)	3.5
	$Mg_{92}Zn_2Al_5Nd_1$	1.94	80	436 (63.3)	476 (69.1)	13.8

20 ALLOYS OUTSIDE THE SCOPE OF THE INVENTION

Commercial Alloy

ZK 60 A-T5

($Mg_{97.7}Zn_{2.1}Zr_{0.2}$) 1.83 50 303 (43.9) 365 (52.9) 11.0

AZ 91 HP-T6

25 ($Mg_{91.7}Al_{8.0}Zn_{0.2}Mn_{0.1}$)

1.83 50 131 (19.0) 276 (40.0) 5.0

EXAMPLE 3

The as-cast ribbon and bulk extruded specimens of rapidly solidified Mg-Al-Zn-X alloys were prepared for transmission electron microscopy by a combination of jet thinning and ion milling. Quantitative microstructural analysis of selected R.S. Mg-Al-Zn-X as cast samples, as shown in Table 3, indicates that the fine grain size ranging from 0.36-0.70 μm and fine cell size ranging from 0.09-0.34 μm of magnesium grains have been obtained by rapid solidification process described herein above. The fine dispersoid

- 16 -

size of magnesium-rare earth or aluminum-rare earth intermetallic compounds ranging from 0.04-0.07 μm is also obtained. Because of high melting point and limited solid solubility, these fine dispersoids of aluminum-rare earth or magnesium-rare earth intermetallic compounds do not coarsen appreciably during high temperature consolidation and are quite effective in pinning the grain boundaries as illustrated in the micrographs in Fig. 2 and the quantitative results in Table 3 for as-extruded samples. Such fine grain and the dispersoid size lead to significant improvements in the mechanical properties as compared to conventionally processed material, as shown in Example 2.

TABLE 3

TEM Microstructure Analysis of Selected
R.S. Mg-Al-Zn-X As-cast and Extruded Samples

No.	Nominal Comp. At (%)	Matrix Grain Size (μm)	Precipitate Sz. Cell Size (μm)	Sz. (μm) MgZn
1	Mg ₉₂ Zn ₂ Al ₅ Ce ₁ (a)	0.56	0.14	0.07
2	Mg ₉₂ Zn ₂ Al ₅ Ce ₁ (b)	0.70	-	0.56
3	Mg _{92.5} Zn ₂ Al ₅ Pr _{0.5} (a)	0.70	0.34	0.15
4	Mg _{92.5} Zn ₂ Al ₅ Pr _{0.5} (b)	0.70	-	0.13
5	Mg ₉₁ Zn ₂ Al ₅ Y ₂ (b)	0.36	-	0.23

TABLE 3 (Contd.)

No.	Precipitate Size (μm) Mg ₁₇ Al ₁₂	Mg ₃ X (X=Ce, Pr)	Al ₂ Y	Volume Fraction (%)
1	-	0.04	-	-
2	0.56	0.04	-	2.33
3	0.15	0.04	-	-
4	0.65	0.03	-	2.02
5	0.23	-	0.04	2.56
	(a) As-Cast	(b) As-Extruded		

- 17 -

EXAMPLE 4

The effect of temperature and strain rate on the tensile properties of the extruded Mg-Al-Zn-X alloys were evaluated in uniaxial tension at a strain rate ranging from about 2×10^{-5} - 2×10^{-3} /sec and at temperatures ranging from ambient to 150°C. Prior to testing, the samples were held at the testing temperature for 30 mins. As compared to room temperature tensile strength of extruded Mg-Al-Zn-X alloys, Y.S. drops to about 38-41 ksi, U.T.S. drops to 44-48 ksi and elongation increase to 50% when sample tested at 100°C at a strain rate of 5.5×10^{-4} /sec. Additional decrease in tensile strength (Y.S. = 16-18 ksi, U.T.S. = 21-22 ksi) accompanied with high elongation (elongation = 200 %) occurred when sample was tested at 150°C. The superplastic behavior (elongation > 100%) of these rare earth containing alloys is due to the fine grain and dispersoid size obtained by the rapid solidification process.

TABLE 4

Elevated Temperature Tensile Properties of
As-Extruded

R.S. Mg-Al-Zn-X Alloy (Strain Rate 5.5×10^{-4} /sec

No.	Composition	Test Temp. (°C)	Y.S.	U.T.S.	Elong.
			MPa (ksi)	MPa (ksi)	(%)
1	Mg ₉₁ Zn ₂ Al ₅ Y ₂	100	287 (41.7)	330 (47.9)	52.3
		150	110 (16.0)	148 (21.5)	219.7
2	Mg ₉₂ Zn ₂ Al ₅ Nd ₁	50	395 (57.4)	444 (64.5)	28.4
		100	258 (37.5)	305 (44.3)	50.3
		150	125 (18.2)	153 (22.2)	199.8

30

The tensile properties of the consolidated article also strongly depend on the strain rate, Table 5. At a constant temperature, increasing the strain rate increases the tensile strength. Moreover, the strain rate dependence of strength increases with increasing temperature. Testing at a high temperature and at a low strain rate tends to

- 18 -

improve the ductility. Superplastic behavior (elongation >100%) occurred at a test temperature of 150°C, and at a strain rate $< 1 \times 10^{-3}$ /sec in the as-extruded bar. The combination of low flow stress (25 ksi yield strength) and high ductility (> 100%) in the alloys of the invention makes them exceptionally useful in superplastic forming such as hot forging. Figure 3 shows two extruded bars of $Mg_{92}Zn_2Al_5Nd_1$ forged at 160°C at a low rate and at 180°C at a moderate rate. Large cracks occurred when the sample was forged at the moderate rate (0.00021 m/sec), Fig. 3(a). Decreasing the ram speed down to 0.00001 m/sec eliminates the cracks in the sample and improves the formability, Fig. 3(b). The mechanical properties of the as-forged sample is about the same as the as-extruded sample, Tables 6, 7. When forged in a close die at a low rate, a complex part may be formed in a single step and with outstanding precision of shape and no cracks. It is to be noted that under the same forging condition severe cracks have been found in the commercial alloy ZK60A.

TABLE 5
The Effect of Temperature and Strain Rate on the
Tensile Properties of
As Extruded R.S. $Mg_{92}Zn_2Al_5Nd_1$ Alloy

Test Temp. (°C)	Strain Rate ($\times 10^{-5}$ /sec)	Y.S.		U.T.S.		Elong. (%)
		MPa	(ksi)	MPa	(ksi)	
20	2.5	398	(57.8)	449	(65.3)	18.0
20	55.0	403	(58.6)	454	(65.9)	11.7
20	250.0	450	(65.4)	497	(72.2)	5.4
50	2.5	332	(48.3)	375	(54.5)	36.1
50	55.0	395	(57.4)	444	(64.5)	28.4
50	250.0	400	(58.1)	449	(65.3)	21.3
100	2.5	169	(24.5)	200	(29.1)	104.5
100	55.0	258	(37.5)	305	(44.3)	50.3
100	250.0	287	(41.7)	338	(49.1)	45.8
150	2.5	58	(8.5)	63	(9.1)	139.6
150	55.0	125	(18.2)	153	(22.2)	199.8
150	250.0	164	(23.8)	200	(29.1)	79.4

- 19 -

TABLE 6

Room Temperature Tensile Properties of
Forged R.S. $Mg_{92}Zn_2Al_5Nd_1$
Extrusion Extruded at Normal Rate

Forged Temp. (°C)	Ram Speed	Cracks	Y.S. MPa (ksi)	U.T.S. MPa (ksi)	Elong. (%)
5					
150	Low	Very small	444 (64.5)	499 (72.5)	10.2
180	Low	None	451 (65.5)	505 (73.4)	12.8
180	High	Large	-----	-----	----
220	High	None	451 (65.0)	516 (75.0)	13.0

TABLE 7

Room Temperature Tensile Properties of
Forged R.S. $Mg_{92}Zn_2Al_5Nd_1$
Extrusion Extruded at Low Rate

Forged Temp. (°C)	Ram Speed	Cracks	Y.S. MPa (ksi)	U.T.S. MPa (ksi)	Elong. (%)
10					
150	Low	Very small	461 (67.0)	523 (76.0)	8.4
160	Low	None	450 (65.4)	512 (74.4)	9.1
15	190	Low	484 (70.3)	540 (78.6)	6.8
210	Low	None	457 (66.4)	510 (74.1)	8.8
220	High	Large	-----	-----	----
230	High	Small	469 (68.1)	536 (77.9)	7.6
240	High	Small	470 (68.3)	529 (76.9)	7.2

EXAMPLE 5

Room temperature tensile properties of 1" diameter extrusions (R.S. $Mg_{92}Zn_2Al_5Nd_1$) made by the present invention were evaluated and compared with the tensile properties of the extrusion made by prior art [S.K. Das and C.F. Chang, U.S. Pat. No. 4,765,954, Rapidly Solidified High Strength Corrosion Resistant Magnesium Base Alloys, August 1988], Table 8. Because of the extensive deformation produced in the extrusion using the method described in the prior art, there is a temperature rise during extrusion. As the result, extrusion made by prior art are effected at higher temperatures, causing coarsening of precipitates and decrease of such mechanical properties as yield strength and ultimate tensile strength, as well as non uniformity of those mechanical properties in the formed product. However, the procedure of superplastic forming minimizes adiabatic heat build-up during extrusion

- 20 -

providing remarkably uniform mechanical properties throughout the extruded article.

TABLE 8

Comparison of Room Temperature Tensile Properties of
1" Diameter Extrusions (R.S. $Mg_{92}Zn_2Al_5Nd_1$)

5 Made by Present Invention and Prior Art

Method of Forming	Section From Front	Y.S. (ksi)	U.T.S. (ksi)	Elong. (%)
Prior Art	0"	67	74	9
	24"	61	68	15
Present	0"	67	74	12
Invention	24"	67	74	13

10 Having thus described the invention in rather
full detail, it will be understood that such detail
need not be strictly adhered to but that further
changes may suggest themselves to one having ordinary
skill in the art, all falling within the scope of the
15 invention as defined by the subjoined claims.

20

25

30

35

- 21 -

We claim:

1. A method of making a superplastic forming
form a consolidated metal article, said article
having been made by compacting a rapidly solidified
5 magnesium based alloy powder consisting essentially
of the formula $Mg_{bal}Al_aZn_bX_c$, wherein X is at least
one element selected from the group consisting of
manganese, cerium, neodymium, praseodymium, and
yttrium, "a" ranges from about 0 to 15 atom percent,
10 "b" ranges from about 0 to 5 atom percent, "c" ranges
from about 0.2 to 3 atom percent, the balance being
magnesium and incidental impurities, with the proviso
that the sum of aluminum and zinc present ranges from
about 2 to 15 atom percent, said alloy having a
15 microstructure comprised of a substantially uniform
cellular network of solid solution phase of a size
ranging from 0.2 -1.0 micron together with
precipitates of magnesium and aluminum containing
intermetallic phases of a size less than 0.1 micron,
20 comprising the step of forming said article at a
forming rate ranging from about 0.00021 m/sec to
0.00001 m/sec.

2. A method as recited by claim 1, wherein said
forming step is carried out at a temperature ranging
25 from about 160 to 275°C.

3. A method as recited by claim 2, wherein said
forming step is an extrusion step.

4. A method as recited by claim 2, wherein said
forming step is a forging step.

30

35

1 / 6

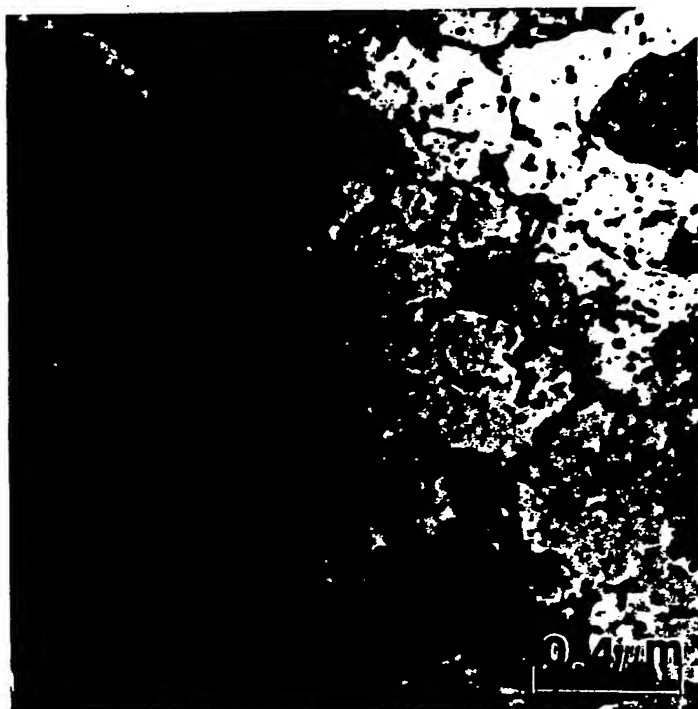


Figure 1(a)

SUBSTITUTE SHEET

2 / 6

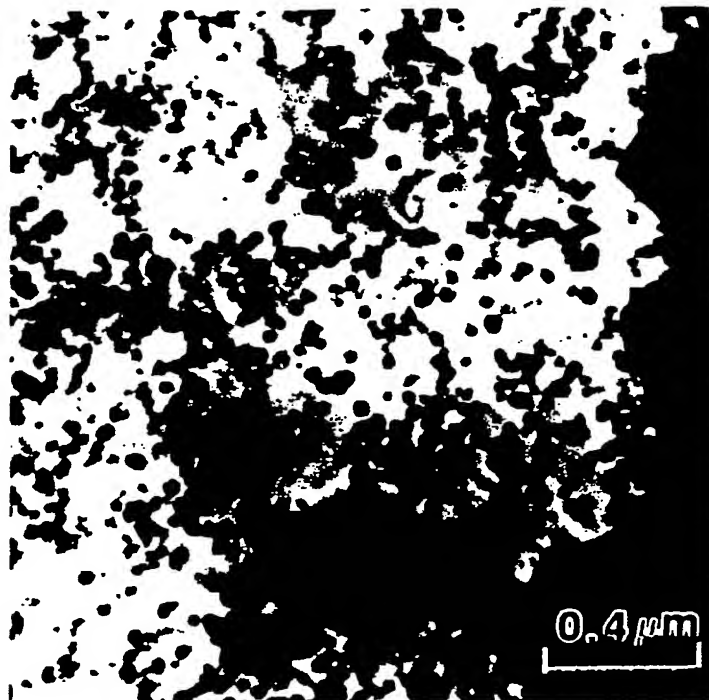


Figure 1(b)

SUBSTITUTE SHEET



Figure 2(a)

SUBSTITUTE SHEET

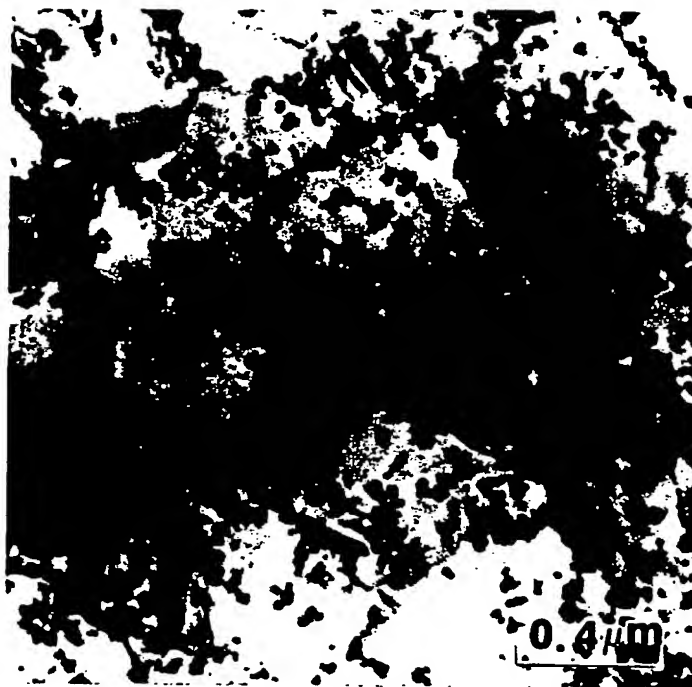


Figure 2(b)

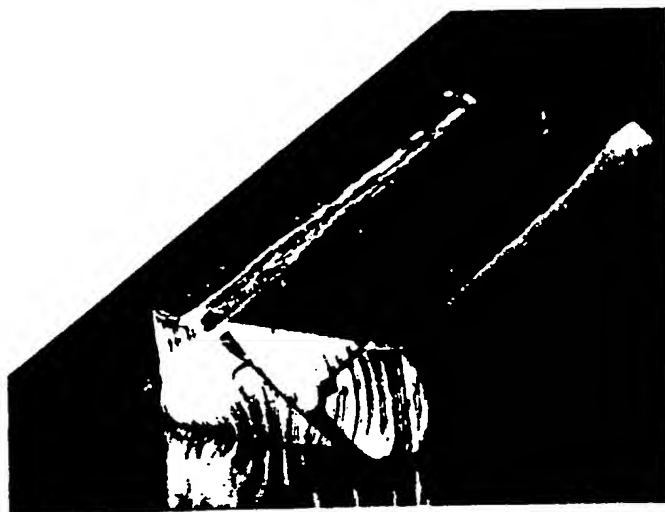


Figure 3(a)

SUBSTITUTE SHEET

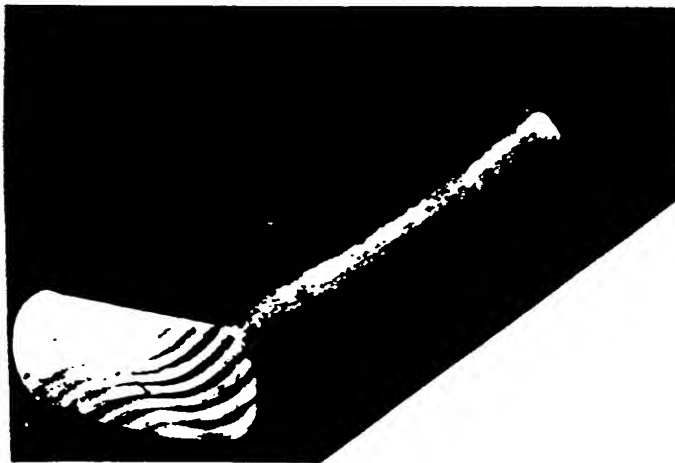


Figure 3(b)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/01048

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 22 C 1/04, C 22 F 1/06		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 22 C, C 22 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0219628 (ALLIED CORP.) 29 April 1987 see claims 1,8; examples of tables I (page 5), II (page 6), III (page 7) cited in the application ---	1
X	WO, A, 89/11552 (ALLIED-SIGNAL INC.) 30 November 1989 see claims 1,2 & US priority 23 May 1988, application serial no. 197796 ---	1,2
A	EP, A, 0104774 (ALCAN INTERNATIONAL LTD.) 4 April 1984 see page 1, lines 1-4; page 7, lines 11-14; claims 2,10 -----	1
<p>¹⁰ Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14th June 1991	31 JUL 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MISS I. TAZELAND	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9101048

SA 45409

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 22/07/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0219628	29-04-87	US-A- 4765954	23-08-88
		JP-A- 62083446	16-04-87
		US-A- 4853035	01-08-89
		US-A- 4857109	15-08-89

WO-A- 8911552	30-11-89	US-A- 4938809	03-07-90
		EP-A- 0417206	20-03-91

EP-A- 0104774	04-04-84	AU-B- 569476	04-02-88
		AU-A- 1846283	28-02-85
		CA-A- 1198656	31-12-85
		GB-A, B 2126936	04-04-84
		JP-A- 59064735	12-04-84
		US-A- 4571272	18-02-86

BLANK PAGE

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

BLANK PAGE